

Process for applying phosphate coatings.

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-  GB2148950 (A)
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-  EP0069950
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Abstract of EP0141341

Zinc or steel surfaces, and in particular galvanised surfaces of external structures such as bridges or gantries, can be protected by application of a composition containing 0.5 to 5 parts zinc, 1 to 20 parts phosphoric acid, 0.01 to 0.5 parts cobalt and/or nickel and an effective amount of an accelerator such as nitroguanidine, sulpho-salicylic acid or sodium nitrobenzenesulphonate.

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(54) Phosphating composition and processes

(57) Zinc or steel surfaces, and in particular galvanised surfaces of external structures such as bridges or gantries, can be protected by application of a composition containing 0.5 to 5 parts zinc, 1 to 20 parts phosphoric acid, 0.01 to 0.5 parts cobalt and/or nickel and an effective amount of an accelerator such as nitroguanidine, sulpho-salicylic acid or sodium nitrobenzenesulphonate.

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SPECIFICATION

Phosphating compositions and processes

5 It is well known that freshly galvanised steel surfaces are difficult to paint satisfactorily unless they are given a pretreatment. Pretreatments for relatively small articles are well known but particular difficulties arise when the articles are large structures such as bridges since it is difficult to achieve thorough cleaning of the surfaces before pretreatment and it is difficult and undesirable to apply a thorough rinse after the pretreatment and before painting. 5

10 Aqueous phosphate solutions have been used for many years for pretreatment of zinc and iron surfaces but they do not wet large structures well, especially because of the poor cleaning of those structures. Zinc phosphate solutions have been widely developed for the pretreatment of smaller articles but generally have to be followed by a thorough rinse. Zinc phosphate solutions that do not require a subsequent rinse are known but are generally only satisfactory if the 10

15 surfaces to which they are applied are very clean. In US Patent Specification 3,346,426 it is described that phosphate coatings can be formed on steel or galvanised surfaces by wiping on a solution containing zinc, phosphoric acid, glycolic acid and sodium 2,4-dinitrobenzenesulphonate. This process does not seem to have been very successful commercially. Commercially, the most widely used process for the pretreatment of 15

20 large galvanised structures is the T-wash process. In this the metal structure is treated with a solution of phosphoric acid and copper carbonate in a mixture of solvents. This composition is relatively easy to apply by brushing onto large structures and it is easy to see where it has been applied. It gives improved paint adhesion compared to freshly galvanised 20

25 zinc but the adhesion is still not entirely satisfactory and the corrosion resistance can be less than would be expected when using a conventional zinc phosphate solution followed by rinsing. 25

30 A composition according to the invention comprises 0.5 to 5 parts zinc, 1 to 20 parts phosphoric acid, 0.01 to 0.5 parts of an additive selected from cobalt and nickel and an effective amount of a non-blistering accelerator, all the parts being by weight. This composition can be formed as a concentrate and diluted with an appropriate amount of solvent to form the 30

35 working solution. The working solution contains sufficient solvent to bring the weight of the composition up to 100 parts by weight. The solvent may consist solely of water or may be a blend of water and organic solvent, typically in an amount of up to 20 parts by weight. The working solution may also contain surfactant, generally in an amount of up to 0.5 parts by weight. A preferred working solution therefore comprises 0.5 to 5% zinc, 1 to 20% phosphoric acid (100%), 0 to 0.5% of cobalt or nickel or a mixture thereof, 0.02 to 0.5% surfactant, an 35

40 effective amount of the accelerator, with the balance being water. The non-blistering accelerator must be one that does not cause substantial blistering of a paint film that is applied over a dried-on, unrinsed, coating of the composition containing the accelerator in an effective, accelerating amount. Blistering is generally associated with the 40

45 accelerator leaving water soluble ionic residues in the coating and so the accelerator preferably is not a highly ionic compound such as sodium chloride or sodium nitrate. Peroxides may be non-blistering but are not preferred because of stability problems and preferred accelerators are organic compounds. The preferred accelerator is nitroguanidine. This needs to be present in an amount of at least 45

50 0.02 parts (0.02% in the working solution) since lower amounts are ineffective. It is usually unnecessary for the amount to be above 1.5 parts and often it is 0.1 to 0.5 parts. Other suitable accelerators are sulpho-salicylic acid (or a salt thereof) and aromatic nitro compounds. The aromatic nitro compound is preferably a nitro benzene sulphonate and generally is sodium nitro benzene sulphonate, or the free acid. Suitable amounts are 0.2 to 1.5 50

55 parts. If the amount is too low, the adhesion of the subsequently applied paint film may be impaired whilst if it is too high there may be excessive blistering of the paint. Preferred amounts are from 0.5 to 1.2%. The solution is preferably substantially free of anions other than the phosphate anions and ions of the three named accelerators or other non-blistering, generally organic, accelerators. It is preferably substantially free of water soluble cations such as alkali metal or ammonia although the amount introduced with, for instance, an aromatic nitro compound, if that is a sodium salt, is acceptable. Preferably the only deliberate additions of cations are the zinc and the cobalt and/or nickel. The compositions may contain a polyhydroxycarboxylic acid, for example, tartaric acid, 55

60 generally in amounts of up to 1% by weight of the working solution. Generally the compositions are free of any other additives. If the amount of zinc is too low, the solution will give inadequate protection while if it is too high there will be a tendency for reduced solution stability and increased blistering of the subsequently applied paint film. Preferably the amount of zinc is between 1 and 4%. 60

65 If the amount of cobalt and/or nickel is too low, it will give negligible improvement in 65

corrosion resistance while if it is too high it may cause the formation of a galvanic corrosion cell with the base metal, and as a result may enhance corrosion. The total amount of cobalt and nickel is generally from 0.05 to 0.4% by weight. Although either metal can be used alone, blends are preferred, generally containing about equal amounts of each.

5 If the amount of phosphoric acid is too low there will be reduced reaction with the metal substrate and decreased adhesion of the phosphated film, and of subsequently applied paint film, and there may be decreased solution stability. If the amount of phosphoric acid is too high there may be excessive attack of the metal surface. Preferably the amount of phosphoric acid is from 4 to 15% by weight.

10 Although it is not essential to include surfactant it is generally desirable, especially when the surface is not entirely clean. Amounts of surfactant of up to 0.5% significantly improve the wettability of the solution on the metal surface without interfering with the phosphating reaction and amounts above 0.5% generally give no further improvement. Often the amount is from 0.05 to 0.3% by weight.

15 Organic solvent is not essential but may facilitate application and wetting properties. Generally the amount is the minimum that gives the desired improvement and is generally below 20% since higher amounts normally give no improvement in application properties and may reduce the stability of the solution to such an extent that the amount of phosphoric acid has to be increased in order to maintain solution stability, this incurring the risk of excessive acid attack on 20 the surface that is being treated.

The surfactant, if present, is preferably a non-ionic surfactant since cationic and amphoteric surfactants may absorb onto the metal surface and inhibit film formation.

The solvent, if present, must be non-toxic to the person applying the composition and must permit the formation of a stable solution. The presence of highly hydrophilic solvents such as 25 methanol is generally undesirable as they tend to cause precipitation of zinc phosphate from the solution. The solvents are therefore preferably moderately polar and many heterocyclic solvents are suitable provided they are not toxic. The preferred solvent is N-methyl-2-pyrrolidone.

Aqueous working solutions free of surfactant and solvent may be difficult to apply and so generally the composition contains either surfactant or solvent or, preferably, both solvent and 30 surfactant.

A process according to the invention comprises applying the working solution onto a zinc or iron surface and allowing it to dry onto the surface. The surface is usually the galvanised surface of an external steel structure such as a bridge or gantry. Application may be by wiping or, preferably, by brushing onto the surface. The surface is preferably substantially free of dirt and 35 grease but it is unnecessary to have cleaned it as thoroughly as is required in conventional zinc phosphate processes. Application is generally at ambient temperature and, since the structure is generally an external structure, in practice this means that application is generally at temperatures of from 3 to 30°C.

35 After the coating has dried a paint coating is normally applied in conventional manner.

40 **Example 1**
As an example of the invention a solution was prepared having the following composition.

Zn	3.0%	45
45 H ₃ PO ₄	12.0%	
Sodium nitro benzene sulphonate	1.0%	
Surfactant	0.1%	
N-methyl-2-pyrrolidone	5.0%	
Co	0.15%	
50 Ni	0.15%	50
Water	to 100.00%	

55 Galvanised panels were treated with this solution at ambient temperature, allowed to dry and overpainted with a chlorinated rubber paint. The panels were subjected to ASTM B117 salt spray and good corrosion protection and paint adhesion were observed.

Various comparative solutions were prepared and used in the same manner. One solution had the same formulation except the nitro benzene sulphonate was omitted. Another solution had the same formulation except the cobalt and nickel were omitted. Another solution had the same formulation except that glycolic acid was added as in US Patent 3,346,426. In other solutions 60 the cobalt and nickel were omitted and were replaced with other transition metals. All these solutions gave inferior results compared to the exemplified solution.

Example 2
The process of Example 1 was repeated using nitroguanidine instead of sodium nitro benzene 65 sulphonate. The amount could be, for instance 0.1%. Although blistering of the paint was not a

major problem in Example 1, this was eliminated in Example 2.

CLAIMS

1. A composition useful in the formation of protective coatings on zinc or iron surfaces and comprising 0.5 to 5 parts zinc, 1 to 20 parts phosphoric acid, 0.01 to 0.5 parts of an additive selected from cobalt and nickel, and an effective amount of a non-blistering accelerator, all the parts being by weight. 5
2. A composition according to claim 1 in which the accelerator is selected from nitroguanidine, sulpho-salicylic acid or a salt thereof and dissolved aromatic nitro compounds. 10
3. A composition according to claim 2 containing 0.02 to 1.5 parts nitroguanidine. 10
4. A composition according to claim 2 containing 0.2 to 1.5 parts sodium nitrobenzenesulphonate or the free acid thereof. 15
5. A composition according to any preceding claim substantially free of other anions or cations. 15
6. A composition according to any preceding claim containing up to 1 part by weight polyhydroxycarboxylic acid. 15
7. A composition according to any preceding claim containing surfactant and/or up to 20 parts by weight organic solvent. 20
8. A composition according to any preceding claim comprising 1 to 4 parts zinc, 0.05 to 0.4 parts cobalt and/or nickel, 4 to 15 parts phosphoric acid, 0.05 to 0.3 parts surfactant and 0 to 20 parts solvent. 20
9. A composition according to any preceding claim including N-methyl-2-pyrrolidone as solvent. 25
10. A composition according to any preceding claim in the form of a working solution diluted with water to make 100 parts by weight. 25
11. A composition according to claim 1 substantially as herein described with reference to either of the examples. 25
12. A process of forming a protective coating on a zinc or iron surface comprising applying a solution according to claim 10 to the surface and allowing it to dry on the surface. 30
13. A process according to claim 12 in which the surface is the galvanised surface of an external steel structure. 30

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